

SMECTITE FORMATION FROM BASALTIC GLASS UNDER ACIDIC CONDITIONS ON MARS

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Introduction: Massive deposits of phyllosilicates of the smectite group, including Mg/Fe-smectite, have been identified in Mars's ancient Noachian terrain [1]. The observed smectite is hypothesized to form through aqueous alteration of basaltic crust under neutral to alkaline pH conditions [2]. These pH conditions and the presence of a CO₂-rich atmosphere suggested for ancient Mars were favorable for the formation of large carbonate deposits [3]. However, the detection of large-scale carbonate deposits is limited on Mars. We hypothesized that smectite deposits may have formed under acidic conditions that prevented carbonate precipitation. In this work we investigated formation of saponite at pH ~4 from Mars-analogue synthetic Adirondack basaltic glass of composition similar to Adirondack class rocks located at Gusev crater. Hydrothermal (200° C) 14 d experiments were performed with and without 10 mM Fe(II) or Mg under anoxic condition [hereafter denoted as anoxic_Fe, anoxic_Mg and anoxic (no addition of Fe(II) or Mg)] and under oxic condition [hereafter denoted as oxic (no addition of Fe(II) or Mg)]. Characterization and formation conditions of the synthesized saponite provided insight into the possible geochemical conditions required for saponite formation on Mars.

Materials and Methods: Adirondack basaltic glass was prepared by melting and quenching procedures in gas mixing furnaces. The powdered mixture of reagent-grade chemicals was melted at 1400°C in a platinum crucible for 12 hours then quenched in water. The obtained glass was reground and melted again. The process was repeated two more times to ensure a homogeneous mixture. The final product was ground and sieved to separate out the ≤ 53 μm particle size. Acetic acid of 100 mM concentration was chosen as a pH 4 buffer. For phyllosilicate formation experiments 15 ml Adirondack suspensions were prepared by mixing 250 mg Adirondack with acetic acid alone or with MgCl₂ or FeCl₂ stock solutions and acetic acid to obtain a final cation concentration of 10 mM. All these samples were prepared under anoxic conditions in a glovebox. In order to determine an effect of O₂ on phyllosilicate formation, an incubation of Adirondack in 100 mM acetic acid was performed under ambient condition. Two replicates were made for every time point (1, 7 and 14 d) in batch reactors (Parr acid digestion vessel). Adirondack basaltic glass after 14 d incubation was examined by X-ray-diffraction (XRD), Mössbauer spectroscopy, visible and near-infrared reflectance spectroscopy (VNIR), scan-

ning electron microscopy (SEM) and electron microprobe analysis to characterize mineralogy, morphology and composition of the synthesized smectite.

Results and Discussion: Mineralogical changes were significant in all samples at the end of experiment. The unaltered Adirondack was composed of 66 wt% X-ray amorphous glass phase, 32 wt% olivine and 2 wt% chromite. After 14d incubation, XRD analysis revealed formation of phyllosilicates based on the 001 peak at ~15 Å (Fig. 1). The weak 001 band could be already detected in the 1 d samples then its intensity increased with increasing reaction time. Smectite was confirmed as the phyllosilicate after treatments with glycerol and KCl and heating to 550°C. The positions of 02l and 060 diffraction bands were indicative of the trioctahedral smectite saponite (Figure 1).

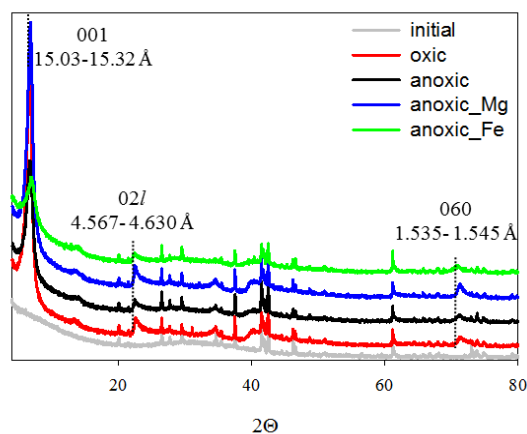


Fig. 1. (a) X-ray powder diffraction patterns of initial and 14 d-incubated synthetic Adirondack glass with peak positions for saponite shown by the dotted lines.

Mössbauer spectroscopy analysis of the 14 d incubated Adirondack suspensions revealed that Fe content in glass was significantly lower than the pristine Adirondack while Fe of olivine remained unchanged. The observed results indicated that smectite formation was due to preferential alteration of the glass, but not olivine. The spectra also displayed smectite Fe(II) and Fe(III) doublets formed during incubation. The smectite doublets were all assigned to Fe(II) and Fe(III) in octahedral coordination in saponite.

Measurements by VNIR revealed compositional differences in octahedral layer of the synthetic saponite.

The band in the 2.25 μm region was assigned to combination stretching and bending modes of $\text{Al(Fe(III),Fe(II))OH}$ while the band near 2.31 μm was due to combination vibrations of $(\text{Mg, Fe(II), Fe(III)})_3\text{OH}$ in saponite (Fig. 2). The band center positions in 2.25 and 2.31 μm areas were affected by Fe oxidation state and shifted to the longer wavelength as the degree of saponite Fe oxidation decreased: 2.246 and 2.312 μm (oxic), 2.249 and 2.317 μm (anoxic), 2.249 and 2.318 μm (anoxic_Mg), 2.252 and 2.323 μm (anoxic_Fe). In addition, the anoxic_Fe sample had a shoulder at 2.352 μm assigned to $(\text{Fe(II)})_3\text{OH}$ combination vibrations of trioctahedral Fe(II) groups.

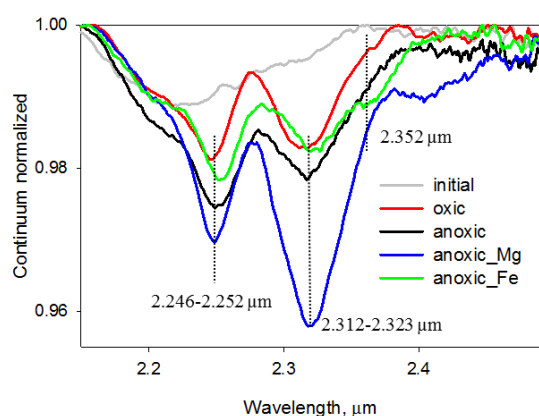


Fig. 2. Continuum normalized reflectance spectra of initial and 14 d-incubated synthetic Adirondack glass with band positions marked with dotted lines.

Results of SEM/EDS of the incubated samples showed the glass surface was covered by a “flaky” coating of the saponite with a distinguishable interface between saponite and glass (Fig. 3). EDS compositional analysis indicated that saponite and glass particles contained Mg, Fe, Na, Ca, Al and Si, however, total Na and Ca content was lower in saponite than in the residual glass. Glass fragments showed evidence of alteration such as formation of cracks and pits on the surface which were not observed on the starting material (Fig. 3).

Microprobe quantitative analysis together with Fe speciation in saponite obtained from Mössbauer analysis was used to evaluate saponite composition. The synthetic saponite contained Si and Al in tetrahedral layers; Al, Mg and Fe $[\text{Fe(II)}+\text{Fe(III)}]$ filled octahedral layer while Na, Ca and K occupied interlayer sites. The total number of octahedral cations was close to 6 [based on $\text{O}_{20}(\text{OH})_4$ stoichiometry] indicating formation of trioctahedral smectite. The ratio of Mg/Fe was close to 1 in oxic, anoxic and anoxic_Mg saponite indicating formation of saponite equally enriched in Mg and Fe. The anoxic_Fe sample had Mg/Fe ratio of 0.43 and 89% Fe(II) indicating formation of Fe(II)-rich saponite.

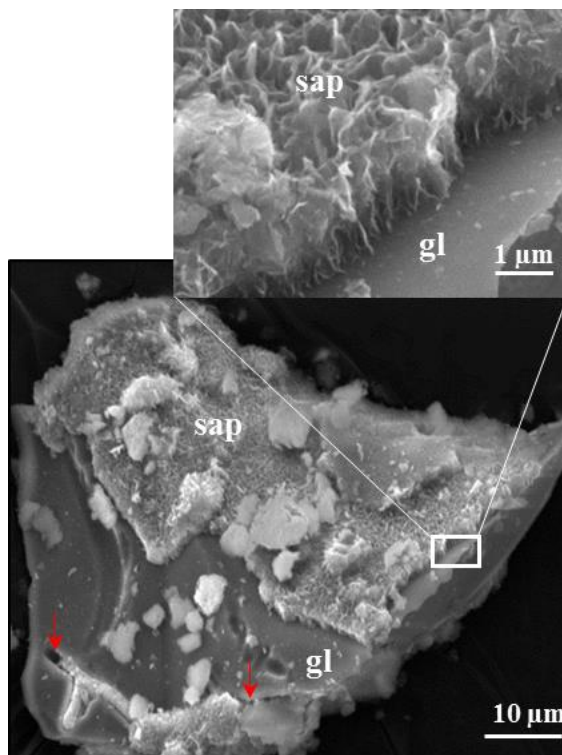


Fig. 3. SEM images of 14 d-incubated anoxic_Fe. Square corresponds to a glass (gl)/saponite (sap) interface area shown at higher magnification. Red arrows point to cracks and pits on the surface of glass.

Conclusions: These experiments showed that Mars-analogue basaltic glass with Adirondack-like composition was altered to saponite under acidic conditions ($\text{pH} \sim 4$) in all experiments. Saponite and smectite minerals in general have thought to have formed under neutral to alkaline conditions during the Noachian era followed by acid-sulfate alteration. The results revealed a new plausible mechanism of smectite formation under acidic conditions on Mars. The lack of the large-scale carbonate detection in Noachian materials supports acidic environment during this era. The principal sources that had potential to contribute significantly to acidity during smectite formation could be elevated atmospheric CO_2 and SO_2 from volcanic process as well as oxidation of Fe(II) originated from igneous minerals and Fe(III) hydrolysis of [3].

References: [1] Murchie S.L. et al.(2009) *JGR-Planets*, 114; [2] Bibring, J.-P. et al. (2006) *Science*, 312, 400-404; [3] Fairén, A. G. et al. (2004) *Nature*, 431, 423-426.